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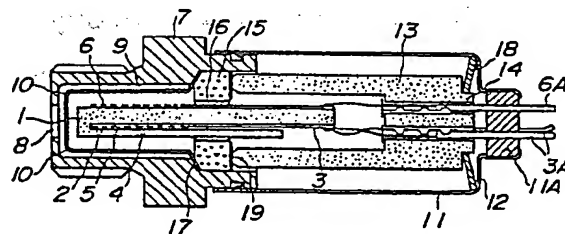
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(54) Electrochemical device, cell and a method of operating the same.

(57) The disclosed electrochemical device uses an electrochemical cell having a solid electrolyte (1) carrying first and second electric conductors (2,6) in contact therewith, and an alternating current is applied to one or both of the electric conductors (2,6) for heating the electrochemical cell by the conductor (2,6) heated by the alternating current, so that the thus heated cell detects or controls concentration of a specific component of a fluid in contact therewith.

A method of operating the same is also disclosed.

FIG. 1



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DESCRIPTION"ELECTROCHEMICAL DEVICE, CELL AND A METHOD OF OPERATING
THE SAME"

This invention relates to an electrochemical cell of simple construction having excellent low-temperature performance characteristics and high durability, and the invention also relates to electrochemical devices including such a cell and to a method of operating the electrochemical cell.

A known electrochemical device for detecting or controlling oxygen concentration in fluids uses an oxygen concentration cell having a solid electrolyte such as a zirconia ceramic, which is an oxygen-ion-conductive solid electrolyte, and electrodes such as platinum electrodes mounted on opposite side surfaces of the solid electrolyte. The principles of such concentration cells have been used in other electrochemical devices such as detectors and pumps for hydrogen, nitrogen, carbon dioxide, sodium, and the like. To ensure satisfactory operation of the electrochemical devices such as the detectors and pumps in a low-temperature gas atmosphere, a variety of methods have been proposed.

For instance, U.S. Patent No. 4,212,720 teaches insertion of a metallic wire heater such as a "Nichrome" wire heater in an internal space of a hollow zirconia ceramic so as to selectively heat the zirconia ceramic, and U.S. Patent No. 4,334,974 teaches provision of a

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heater which is attached via an insulating layer to one side surface of a planar oxygen concentration cell so as to selectively heat the oxygen concentration cell.

However, the electrochemical devices of the prior art have shortcomings in that their construction is complicated, their durability is low and their output voltages are susceptible to error due to deterioration of the solid electrolyte and the insulating layer by solid phase reactions therebetween at elevated temperatures and due to deterioration of the insulation resistance of the insulating layer at elevated temperatures.

An aim of the present invention is to reduce the above shortcomings.

According to the present invention there is provided an electrochemical cell having a solid electrolyte and first and second electric conductors, characterised in that the first electric conductor is in direct contact with the solid electrolyte, the second electric conductor, which is to be exposed to a fluid including a component to be detected or controlled, is in direct contact with the solid electrolyte at a spacing from the first electric conductor, and in that means are provided to connect an AC power source across at least one of said first and second electric conductors, whereby said electrochemical cell can be heated, in use, and when heated be used to detect and/or control the concentration of the component of the fluid in contact therewith which component causes an electrode reaction at the electrochemical cell.

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The invention also provides an electrochemical cell including an electrolytic cell and a concentration cell, characterised in that the electrolytic cell consists of a pair of electrodes secured to respective
5 surfaces of a solid electrolyte and the concentration cell consists of a pair of electrodes secured to respective surfaces of the solid electrolyte or another solid electrolyte electrically conductively connected thereto; in that a heater made of a conductor is secured
10 to the or one of the solid electrolytes or to a further solid electrolyte electrically conductively connected thereto; and in that a cavity or porous layer is adjacent a surface of the or each solid electrolyte with electrodes thereon, and allows access to such surface(s)
15 with a given diffusion resistance of a fluid to be detected, one electrode of each of the electrolytic and concentration cells being provided so as to face the cavity or porous layer.

In another aspect the invention provides a
20 method of operating an electrochemical cell having first and second spaced electric conductors tightly secured to a solid electrolyte with one conductor being exposed to a fluid including a component to be detected or controlled, characterised by the step of passing an alternating
25 current through at least one of said electric conductors so as to heat the electrochemical cell, and detecting or controlling the concentration of that component, which component causes an electrode reaction at said

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electrochemical cell.

The present invention is based on the discovery that if a solid electrolyte is heated by thermal energy generated in an electric conductor in direct contact with
5 the solid electrolyte through application of an alternating current thereto, preferably an alternating current at a frequency higher than a certain value, then no electrolysis occurs in the solid electrolyte and no deterioration of the solid electrolyte is caused. Also,
10 such electric conductor can be used as an electrode of an electrochemical cell formed of the solid electrolyte, which cell can be used in a concentration cell or a pump for certain substances.

The invention will be more clearly understood
15 from the following description which is given by way of example only with reference to the accompanying drawings, in which:

Fig. 1 is a schematic sectional view of an oxygen concentration detector which is an embodiment of
20 electrochemical device according to the present invention;

Fig. 2 is an exploded perspective view of the

essential portion of the oxygen concentration detector of Fig. 1, showing its mechanical construction and electric connection;

05 Figs. 3 and 4 are electric equivalent circuit diagrams of an electrochemical device according to the present invention;

Fig. 5 is a graph showing the complex impedance characteristics of an electrochemical cell according to the present invention;

10 Figs. 6 through 8 are exploded perspective views, showing mechanical constructions and electric connections of three different embodiments of electrochemical device of the invention;

15 Fig. 9 is a perspective view of another embodiment of the invention which uses a tubular solid electrolyte;

Fig. 10 is an exploded perspective view of another oxygen concentration detector according to the present invention, showing the mechanical construction and electric connection thereof;

20 Figs. 11-13 are perspective views of other embodiments of the invention; and

Fig. 14 is a graph showing the operation properties of the oxygen concentration detector of the invention.

25 Throughout different views in the drawings, numeral 1 is a solid electrolyte, 2 is a first electric conductor, 3 is a third electric conductor, 3' is an end

portion with a protruded conductor in a through hole, 3A and 6A are terminals, 4, 25, and 36 are gastight layers, 5 is a hollow space, 6 and 6' are second electric conductors, 7 is a housing, 8 and 10 are openings, 9 is
05 a heat insulating cylinder, 11 is a cap, 11A is a plug, 12 is a venthole, 13 is an insulator, 14 is a hole, 15 is a flange, 16 is a glass layer, 17 is a seal, 18 is a spring, 19 is a metallic washer, 20 is an AC power source, 21 is a potentiometer, 22 is a porous
10 protective layer, 23 is a porous ceramic layer, 24 is an anode, 25A is a window, 26 is a reference electrode, 27 and 33 are capacitors, 28 is a diode, 29 and 32 are resistors, 30 is an inductor, 31 is an AC ammeter, 31D is a DC ammeter, 34 is a DC power source, 35 is a
15 switch, 37 is a gas diffusing hole, 38 is a cavity, 39 is a protruded conductor of the end portion 3', 40 is a porous layer, 41, 42, 47 and 48 are electric conductors, 43 and 46 are solid electrolytes, 44 is a porous ceramic body and 45 is a gas diffusion hole.

20 Referring to Fig. 1 showing an oxygen concentration detector as an embodiment of the electrochemical device of the invention and Fig. 2 showing an exploded view of an electrochemical cell in the detector of Fig. 1, a solid electrolyte 1 is made of zirconia
25 ceramics containing added yttria. A first electric conductor 2 made of platinum is disposed on one side surface of the solid electrolyte 1 in direct contact therewith, and third electric conductors 3 are

connected to opposite ends of the first electric conductor 2 so as to facilitate application of an AC voltage to the first electric conductor 2. The first electric conductor 2 acts both as a heater wire and a
05 reference electrode of the oxygen concentration cell of the oxygen concentration detector, and the surface of the first electric conductor 2 is exposed to a fluid in a hollow space 5 defined between the solid electrolyte 1 and a gastight layer 4. A second electric conductor 6
10 made of platinum is disposed on the other side surface of the solid electrolyte 1 so as to form an electrode for a gas being measured. Thus, as an embodiment of the electrochemical cell of the invention, an oxygen concentration cell is defined by the solid electrolyte 1
15 having the first electric conductor 2 and the second electric conductor 6 mounted on opposite side surfaces thereof.

A housing 7 with an opening 8 and a heat insulating cylinder 9 with openings 10 enclose that end
20 of the oxygen concentration cell which holds the second electric conductor 6 and the first electric conductor 2 disposed on the opposite surfaces of the solid electrolyte 1. A gas to be measured reaches the surface of the second electrode 6 through the opening 8 of the
25 housing 7 and the openings 10 of the heat insulating cylinder 9. The other end of the oxygen concentration cell is enclosed by a cap 11 with ventholes 12 and an insulator 13 made of alumina ceramics with a hole 14,

so that the air acting as a reference gas for the oxygen concentration detector of Fig. 1 reaches the surface of the reference electrode formed of the first electric conductor 2 through the venthole 12 of the cap 11 and the hole 14 of the insulator 13. The cap 11 snugly engages the housing 7 as shown in the figure.

The housing 7 holds the oxygen concentration cell by a supporting flange 15 which engages the oxygen concentration cell with a glass layer 16 inserted therebetween.

A seal 17 is packed in the space between the inside surface of the housing 7 and the flange 15, so that the gas to be measured is separated from the air by the combination of the flange 15, the glass layer 16, and the seal 17. To ensure the gastightness of the seal 17, a spring 18 secured to the inside surface of the cap 11 urges the insulator 13 and the flange 15 against the seal 17 held by the inside surface of the housing 7. A metallic washer 19 is inserted between the insulator 13 and the flange 15. The second electric conductor 6 and the third electric conductors 3 are connected to corresponding terminals 6A and 3A through lead wires, and a plug 11A fitted in one end of the cap 11 holds the terminals 6A and 3A.

When an AC power source 20 is connected to opposite ends of the first electric conductor 2 through capacitors 27 and the third electric conductors 3 as shown in Fig. 2, Joule heat is generated in the first electric conductor 2 by the alternating current from

the AC power source 20, and the Joule heat thus generated acts to heat the solid electrolyte 1 in direct contact with the conductor 2. When the temperature of the solid electrolyte 1 rises to a certain level, it becomes oxygen-ion-conductive and a part of the alternating current in the first electric conductor 2 leaks into the solid electrolyte 1. It is noted that such leakage of the alternating current does not affect the DC component of the potential difference produced between the first electric conductor 2 and the second electric conductor 6 of the oxygen concentration cell, because as long as the positive half cycle and the negative half cycle of the alternating current leaking into the solid electrolyte 1 are symmetrical relative to the zero point of the alternating current, such alternating current does not cause any substantial chemical reaction at the interface between the first electric conductor 2 and the solid electrolyte 1. Accordingly, the oxygen concentration of the gas being measured can be accurately detected by measuring the DC component of the potential difference between the first electric conductor 2 and the second electric conductor 6 of the oxygen concentration cell by a potentiometer 21 while maintaining the alternating current through the first electric conductor 2 and the solid electrolyte 1. In this case, oxygen contained in the gas being measured is an example of that component of fluid being measured which component causes an electrode reaction, and the thus caused

electrode reaction produces the above-mentioned DC component of the potential difference between the electric conductors 2 and 6. Preferably, the resistance of the third electric conductors 3 acting as the lead
05 wires for passing the alternating current is smaller than the resistance between opposite ends of that portion of the first electric conductor 2 which is in contact with the predetermined heatable portion of the solid electrolyte 1, so that outside the predeter-
10 mined heatable portion the solid electrolyte should not be heated and any error of the electromotive force of the oxygen concentration cell due to the heating of such outside should be avoided.

Instead of the potentiometer 21, a DC power
15 source can be connected across the first electric conductor 2 and the second electric conductor 6, so that oxygen is transmitted for instance from the second electric conductor 6 to the first electric conductor 2 in proportion to the amount of electric charge from the
20 DC power source. In this case, the electrochemical cell can be used either as an oxygen pump or an oxygen concentration detector based on the principle of diffusion current caused by the above-mentioned transmission of oxygen.

25 The behavior of the alternating current passed to the first electric conductor 2 will be described now in further detail.

Fig. 3 shows an electric equivalent circuit

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of a heat generating portion consisting of the first electric conductor 2 and the solid electrolyte 1.

In the figure, C_1 is an electrostatic capacitance component representing polarization at the interface

05 between the first electric conductor 2 and the solid electrolyte 1, R_1 is a polarization resistance component at the interface between the first electric conductor 2 and the solid electrolyte 1, C_2 is an electrostatic capacitance component due to the grain boundaries of the solid electrolyte 1, R_2 is a resistance component
10 due to the grain boundaries of the solid electrolyte 1, R_3 is a resistance component representing resistances of the crystal grains of the solid electrolyte 1, and R_4 is the resistance of the first electric conductor 2.

15 In reality, the constants of the equivalent circuit of Fig. 3 are divided into a large number of similarly defined constants C_1' , R_1' , C_2' , R_2' , and R_3' relating to individual crystal grains constituting the solid electrolyte 1, and such divided constants are
20 connected to resistances R_4' of constituent sections of the first electric conductor 2 in a more complicated manner as shown in Fig. 4.

The frequency characteristics of the equivalent circuit of Fig. 3 can be expressed by a complex impedance
25 formula $Z = Z' - jZ''$ which can be plotted as a curve including two continuous arcuate portions as shown in Fig. 5. In the figure, the resistance value of the point A corresponds to the quantity of $R_4(R_1 + R_2 + R_3) / (R_1 + R_2 + R_3 + R_4)$,

the resistance value of the point B corresponds to the quantity of $R_4(R_2+R_3)/(R_2+R_3+R_4)$, and the resistance value of the point C corresponds to the quantity of $R_3 \cdot R_4/(R_3+R_4)$. The polarization from the point A to the point B on the frequency characteristics curve of Fig. 5 is mainly due to the resistance components R_1 , R_2 , R_3 , and R_4 and the capacitance components C_1 and C_2 , while that from the point B to the point C is mainly due to the resistance components R_2 , R_3 , and R_4 and the capacitance component C_2 . As regards the variation of the complex impedance characteristics with the frequency variation, the point A represents DC, and as the frequency increases, the complex impedance varies along the arcuate locus toward the point B and further along the arcuate locus toward the point C.

When a direct current or an alternating current at a low frequency in the neighbourhood of the point A of Fig. 5 is applied to the first electric conductor 2, most of the current flows through the resistance components R_4 and R_1 , and only little of it flows through the capacitance component C_1 . The polarization due to the resistance component R_1 is usually non-linear and has poor symmetry. If this polarization is too large, decomposition of the solid electrolyte and the peeling of the electric conductors can be caused, and the durability and the accuracy of measurement of the electromotive force are deteriorated.

When an alternating current at a frequency in

the neighbourhood of the point B or higher than that of the point B is passed to the first electric conductor 2, the interface impedance between the electric conductor 2 to which the alternating current is passed and the solid electrolyte 1 becomes largely independent of the interface capacitance between the electric conductor to which the alternating current is passed and the solid electrolyte and the alternating current flows mainly through the resistance component R_4 and the capacitance component C_1 , and only little of it flows through the resistance component R_1 . More particularly, in this case, the polarization due to the alternating current through the solid electrolyte mainly consists of the polarization in the inside of the solid electrolyte, so that the alternating current hardly contributes to electrode reactions and excellent durability and accurate measurement of the electromotive force can be ensured.

The frequency for the point B of Fig. 5 varies depending on the kind, micro structure, temperature, and shape of the solid electrolyte used. For instance, in the case of a 1 mm thick zirconia ceramics electrolyte having a chemical composition of $(ZrO_2)_{0.94}(Y_2O_3)_{0.06}$ and containing 1 weight % of clay, which electrolyte has the electric conductors mounted thereon as shown in Fig. 2, the frequency of the point B is 50 Hz at 350°C and 3 kHz at 600°C.

Furthermore, in the case of an oxygen concentration detector having a solid electrolyte consisting

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of zirconia ceramics with electric conductors made of platinum mounted to the ceramics as shown in Fig. 1, the resistance component R_4 of the electric conductor at the generally used operating temperature of about 600°C is about 10^1 ohms and the sum of the resistances (R_2+R_3) of the crystal boundaries and the crystal grains of the solid electrolyte at about 600°C is about 10^4 ohms, so that the heat generated in the solid electrolyte by the alternating current flowing through the solid electrolyte is very small.

Examples of the solid electrolyte to be used in the device and cell according to the present invention are the above-mentioned zirconia ceramics, β -alumina, aluminium nitride, NASICON (i.e. $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$), SrCeO_3 , solid solutions of Bi_2O_3 , oxides of other rare earth elements, $\text{La}_{1-x}\text{Ca}_x\text{YO}_{3-\alpha}$, and the like. As to the material of the electric conductors, metals such as nickel, silver, gold, platinum, rhodium, palladium, iridium, ruthenium, tungsten, molybdenum, and the like, or alloys thereof are preferable because of their high durability, but compounds such as zinc oxide, LaCrO_3 , LaB_6 , SiC , and the like can be also used.

In order to securely fix the electric conductors to the solid electrolyte, a variety of methods are available; for instance, vacuum evaporation, sputtering, electroless plating, pyrolysis or reduction of a solution of salt of metal, baking of paste, cermet or flame spray, or other known methods for mounting

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electrodes to ceramics or the like. To prevent the evaporation and contamination of the electric conductors during operation, the electric conductors can be protected by heat-resisting coating or by embedding the electric conductor in the solid electrolyte. Preferably, fine powder of zirconia, alumina, or the like is mixed in the material of the electric conductors, so as to regulate the resistance of the electric conductors and to prevent the electric conductors from being peeled off or broken due to firing during operation.

The application of the alternating current to the electric conductor can be effected either continuously or intermittently for instance by using a switch 35 of Fig. 6. The switch 35 alternately connects the AC power source 20 and the potentiometer 21 to the electrochemical cell so as to alternately heat the solid electrolyte and detect the electromotive force produced therein.

In the device of the invention, it is possible to accurately measure the temperature of the electrochemical cell with excellent response to temperature change by measuring the impedance as seen from the opposite ends of the electric conductor, which impedance is a composite of the temperature-sensitive resistance of the electric conductor and the temperature-sensitive impedance of the solid electrolyte.

The construction of the electrochemical cell according to the present invention is not restricted to

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that of Fig. 2. For instance, in the embodiment of Fig. 6, a solid electrolyte 1 has a first electric conductor 2 secured to one side surface thereof and a second electric conductor 6' secured to the opposite side surface thereof, and the two electric conductors 2 and 6' are connected in series and an alternating current is passed to the serial conductors 2 and 6' from an AC power source 20. A porous protective layer 22 is disposed on that surface of the solid electrolyte 1 which carries the second electric conductor 6' in tight contact therewith, so that a gas to be measured can come in contact with the second electric conductor 6' secured to the solid electrolyte 1. On the other hand, a porous ceramic layer 23 is disposed on the opposite side surface of the solid electrolyte 1 carrying the first electric conductor 2, and the outer surface of the porous ceramic layer 23 is covered by a gastight layer 4, so that a reference gas is brought in contact with the first electric conductor 2 secured to the solid electrolyte 1.

Fig. 7 shows a different embodiment of the invention, in which a first electric conductor 2 made of tungsten, a second electric conductor 6 acting as an electrode for a gas to be measured, and an anode 24 are all disposed on the same side surface of a solid electrolyte 1. A gastight layer 25 made of a solid electrolyte and having a window 25A is disposed on the solid electrolyte 1 so as to cover the first electric conductor 2

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and third electric conductors 3 connected thereto. A porous protective layer 22 covers the entire second electric conductor 6 through the window 25A of the gastight layer 25, the entire anode 24, and a part of
05 the gastight layer 25. A small direct current is applied across the first electric conductor 2 and the anode 24, so that the first electric conductor 2 is polarized into a cathode. Desired concentration of a component of the gas being measured can be determined
10 by measuring the potential difference between the first electric conductor 2 and the second electric conductor 6.

Fig. 8 shows an embodiment of the invention, in which a first electric conductor 2 is embedded in a solid electrolyte 1. More particularly, three solid
15 electrolyte layers 1 are used, and a first electric conductor 2 with third electric conductors 3 connected to opposite ends thereof is sandwiched between the top layer 1 and the central layer 1, while a reference electrode 26 made of Ni-NiO mixture is sandwiched
20 between the central layer 1 and the bottom layer 1, so that the first electric conductor 2 and the reference electrode 26 are embedded in the solid electrolyte 1 when the three layers thereof are joined one over the other.. A second electric conductor 6 is disposed on
25 the top surface of the solid electrolyte 1 as seen in Fig. 8, and a gas to be measured comes in contact with the second electric conductor 6 through a porous protective layer 22. A gastight layer 4 covers the third

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electric conductors 3 so as to seal them against the gas to be measured. An end portion 3' of the second electric conductor 6 has a protrude conductor 39 (dotted line) extending through a hole (not shown) of the top solid electrolyte layer 1 so as to complete an electric connection to one of the third electric conductors 3. An alternating current is applied from an AC power source 20 to the first electric conductor 2 through the third electric conductors 3. The desired measurement can be taken by measuring the potential difference between the second electric conductor 6 exposed to the gas being measured and the reference electrode 26 by a potentiometer 21 connected to the reference electrode 26 and the end portion 3' of the second electric conductor 6 through the third electric conductor 3.

In the present invention, a plurality of electrochemical cells provided in one solid electrolyte can be heated by passing alternate current into a conductor secured on said solid electrolyte and in this case, in order to avoid the interference between the respective electrochemical cells, for example an electrochemical cell which forms an electrolytic cell which controls concentration of fluid components concerning electrode reaction and an electrochemical cell which forms a concentration cell, which detects concentration of said components, it is desirable to use the following electrochemical cells.

Firstly is an electrochemical cell which comprises

an electrolytic cell consisting of a pair of electrodes secured to both surfaces of a first layer-formed solid electrolyte, a concentration cell consisting of a pair of electrodes secured to both surfaces of a second
05 layer-formed solid electrolyte, which is electrically conductively laminated to the first solid electrolyte, a heater made of a conductor which is secured to the first or second solid electrolyte or a solid electrolyte electrically conductively connected thereto (said heater may
10 act the function of electrode of the electrolytic cell or concentration cell), and a cavity or a porous layer which is provided between the first solid electrolyte and the second solid electrolyte and connects to the outside through a porous body or a hole having a given diffusion
15 resistance against a fluid to be detected, one electrode of the electrolytic cell being provided so as to face said cavity or porous layer, one electrode of the concentration cell being provided so as to face said cavity or porous layer or being the same as the electrode
20 of the electrolytic cell facing the cavity or porous layer, and other electrodes of the electrolytic cell and the concentration cell which do not face the cavity or porous layer being provided at an opposite side with respect to the electrode of the electrolytic
25 cell facing the cavity or porous layer by inserting the first and second solid electrolytes.

A further electrochemical cell comprises an electrolytic cell consisting of a pair of electrodes

secured to both surfaces of a layer-formed solid electrolyte, a concentration cell consisting of a pair of electrodes secured to both surfaces of said solid electrolyte, a heater made of a conductor which is
05 secured to the solid electrolyte or a solid electrolyte electrically conductively connected thereto-(said heater may act the function of an electrode of the electrolytic cell or concentration cell) and a cavity or porous layer, which is provided on one surface of the solid electrolyte
10 and connects to the outside through a porous body or a hole having a given diffusion resistance against a fluid to be detected, one electrode of the electrolytic cell being provided so as to face the cavity or porous layer, one electrode of the concentration cell being
15 provided so as to face the cavity or porous layer, and the maximum value of DC resistance between the separated electrodes positioned on the common side of the solid electrolyte being larger than the DC resistance between the electrodes of the electrolytic cell.

20 Figs. 11-13 are other embodiments of the invention and are exploded perspective views of oxygen concentration detectors provided in solid electrolytes in which an oxygen pump and an oxygen concentration cell are integrally disposed in a structure so that the
25 relative interference is low.

In Fig. 11, one side surface of a solid electrode 1 made of zirconia ceramics is provided with a porous platinum conductor 41, which is the cathode of the

oxygen pump and also an electrode for gas being measured in the oxygen concentration cell, and a platinum-rhodium alloy conductor 2 which is a heater surrounding the conductor 41. A part of the conductor 41 connects to a gas being measured through a porous zirconia ceramic layer 40 and the other part of the conductor 41 and the conductor 2 are tightly sealed between the solid electrolytes 1 and 4. Another surface of the solid electrolyte 1 is provided with a porous platinum conductor 6, which is the anode of the oxygen pump, and a porous platinum conductor 42 which is another electrode of the oxygen concentration cell. The conductor 6 and the conductor 42 are exposed to a cavity 5 provided in a zirconia ceramics gastight layer 4 and are separately arranged at such a position that DC resistance between the conductor 6 and the conductor 42 is larger than DC resistance between the conductor 6 and the conductor 41. An alternating current of a frequency of 10 KHz is passed to both terminals of the conductor 2 from AC power source 20 to heat the solid electrolyte. Direct current is passed from DC power source 34 between the conductor 41 and the conductor 6 to make oxygen concentration at the interface between the porous layer 40 and the conductor 41 substantially zero. The oxygen concentration at the interface between the porous layer 40 and the conductor 41 is detected by a potentiometer 21 as an electromotive force of the oxygen concentration cell which is formed by the conductor 41, the solid electrolyte 1 and the

conductor 42. The electromotive force in this case is shown by curves B and B' in Fig. 14 and is smaller in influence upon the electromotive force due to direct current flowing to the oxygen pump than a curve A showing the potential difference between the conductor 6 and the conductor 41 which form the oxygen pump. It is not necessary to vary a threshold value of the electromotive force for detecting the oxygen concentration depending upon a value of the pump electric current and the detecting circuit can be simplified.

Fig. 12 is an exploded perspective view of an oxygen concentration detector which makes the influence of the electric current of the oxygen pump upon the electromotive force of the oxygen concentration cell smaller. One side surface of zirconia ceramic solid electrolyte 1 is provided with a porous platinum conductor 6 which is the anode of the oxygen pump and a surface of the conductor 6 is covered with a spinel porous protective layer 22. A lead wire portion of the conductor 6 is covered with zirconia ceramic gastight layer 4. Another surface of the solid electrolyte 1 is provided with a porous platinum conductor 41 which acts as a cathode of an oxygen pump together with an electrode for gas being measured of an oxygen concentration cell, and a platinum-rhodium alloy conductor 2 which becomes a heater and the conductor 41 are connected to a middle point of the conductor 2.

The conductor 41 is exposed to a cavity 38

provided in zirconia ceramic solid electrolyte 25 and the cavity 38 connects to a gas being measured through zirconia ceramic porous body 44 having a given gas diffusion resistance which is provided at one end of zirconia ceramic solid electrolyte 43. A porous platinum electrode 42 which is a reference electrode of the oxygen concentration cell is provided on a surface of the solid electrolyte 43 placed at an opposite side to the anode conductor 6 with respect to the cathode conductor 41 and the conductor 42 is exposed to a cavity 5 provided in zirconia ceramic gastight layer 4. Both terminals of the conductor 2 are connected to an AC power source of a frequency of 30 KHz through conductors 3 of lead portions and an inductor 30 to heat the solid electrolytes 1, 25 and 43.

Between the conductor 6 which is the anode of the oxygen pump and the conductor 41 which is the cathode is connected DC power source 34 to pass direct current and make the oxygen concentration in the cavity 38 substantially zero.

The electromotive force of the oxygen concentration cell formed by the conductor 41, the solid electrolytes 25 and 43 and the conductor 42 is shown by curves C and C' in Fig. 14. The influence of the oxygen concentration cell on the electromotive force is smaller than that of Fig. 11 and the oxygen concentration can be more accurately detected without varying the threshold value of the electromotive force.

Fig. 13 is an embodiment of oxygen concentration detector which further lowers the impedance of the oxygen concentration cell and can more easily measure the electromotive force than the detector of Fig. 12.

05 One side surface of zirconia ceramic solid electrolyte 1 is provided with a porous platinum conductor 6 which is the anode of oxygen pump and the surface of the conductor 6 is coated with zirconia porous layer 23.

10 Another surface of the solid electrolyte 1 is provided with a porous platinum conductor 41 which is the cathode and has a larger area than the conductor 6, opposing to the conductor 6. The conductor 41 faces a cavity 38 formed in zirconia ceramic solid electrolyte 25. The cavity 38 connects to the gas being
15 measured through gas diffusing holes 37 and 45. At the opposite side of the cavity 38 to the conductor 41, there is provided a porous platinum electrode 47, which is an electrode for gas being measured of an
20 oxygen concentration cell provided on one side surface of a solid electrolyte 46. The conductor 47 is connected to the conductor 41 through platinum conductor 48 connecting both sides of the solid electrolyte 25 passing through a side surface of the cavity 38 and
25 also connected to a middle point of the conductor 2. A conductor 42 which is a reference electrode of the oxygen concentration cell is provided opposing to the conductor 47 by inserting the solid electrolyte 46

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between the conductor 42 and the conductor 47, and is exposed to a cavity 5 provided in zirconia gastight layer 4. Alternating current of a frequency of 1 KHz is passed to both terminals of the conductor 2 which is a heater, through a conductor 3 and an inductor 30 from AC power source 20 to heat the solid electrolytes 1, 25 and 46 and direct current is passed into the conductor 6 and the conductor 41 through the conductor 3 which is lead wires to control the oxygen concentration in the cavity 38 to substantially zero.

The oxygen concentration in the cavity 38 is detected by measuring the electromotive force of the oxygen concentration cell constructed with the conductors 42, 47 and the solid electrolyte 46, with a potentiometer 21.

In this construction, the conductor 41 is larger than the conductor 6 in area and the conductors 2, 42 and 47 are arranged in such a position that these conductors are DC sealed to the conductor 6, so that the amount of the pump current to the conductors 2, 42 and 47 is low and the opposing area of the conductors 42 and 47 forming the oxygen concentration cell is large, so that the impedance of the oxygen concentration cell can be lowered and an oxygen concentration cell having low noise and fast response rate can be obtained.

The shapes of the solid electrolyte 1, and the first and second electric conductors 2 and 6 are not restricted to be planar as shown in the preceding

embodiments. In fact, the solid electrolyte 1 can be tubular with or without a bottom, and the first electric conductor 2 can be spiral, and the second and third electric conductors 6 and 3 can be curved, as shown in
05 Fig. 9.

In passing the alternating current to the electrochemical cell of the invention while taking measurement of the electromotive force thereof or feeding the direct current thereto for electrolysis,
10 the number of lead wires from the power source to the electrochemical cell can be reduced by using a capacitor 27 as shown in Figs. 2 and 10. Such capacitor 27 isolates the alternating current from the DC circuitry for measuring the electromotive force of the electro-
15 chemical cell or for applying the direct current for electrolysis. The DC power source for electrolysis can be dispensed with by using a combination of a diode 28 and a resistor 29 for rectifying the current from the AC power source 20, as shown in Fig. 7.

20 Referring to Fig. 10, if an AC power source 20 producing rectangular waves or pulses is used, it is preferable to insert an inductor 30 in series with the AC power source 20, so as to prevent induction noise due to harmonics.

25 The temperature of the electrochemical cell can be detected by measuring the alternating current through it by an AC ammeter 31, because the temperature characteristics of the impedance of the electrochemical

cell is known. To prevent erroneous operation due to leakage of an AC current to the potentiometer 21, a filter circuit formed of a resistor 32 and a capacitor 33 may be connected to the potentiometer 21.

05 The invention will be described in further detail now by referring to examples.

Example 1

 A 1 mm thick planar body was prepared by using a mixture consisting of 100 parts by weight of powder material containing 97 mole % of zirconia (ZrO_2) and 3 mole % of yttria (Y_2O_3), 1 part by weight of alumina (Al_2O_3) as a sintering aid, and 12 parts by weight of binder including 8 parts by weight of polyvinyl butyral and 4 parts by weight of dioctyl phthalate.

15 Referring to Fig. 7, a first electric conductor 2 and alternating current receiving terminals thereof formed of third electric conductors 3 were printed on one side surface of the thus prepared planar body by the screen printing method while using a mixture containing 90 parts by weight of tungsten powder and 10 parts by weight of alumina powder. A windowed gastight layer 25 having the same chemical composition as that of the planar body was applied selectively on said one side surface of the planar body by the screen printing method, so as to cover the entire first electric conductor 2 and most of the third electric conductors 3 with the gastight layer 25, and the thus printed planar body was sintered at $1,400^\circ C$ in a hydrogen atmosphere

furnace for making the solid electrolyte 1. A second electric conductor 6 and an anode 24 both made of platinum were deposited on said one side surface of the solid electrolyte 1 at the positions as shown in Fig. 7
05 by the high-frequency sputtering method. A porous protective layer 22 made of spinel was coated on the second electric conductor 6, the anode 24, and the gastight layer 25 by the plasma flame spray method. Thus, an oxygen concentration detector according to
10 the present invention was produced. In this detector, the electric resistance of the first electric conductor 2 at room temperature was 1.2 ohm and that of the third electric conductors 3 forming the terminals of the first electric conductor 2 at room temperature was
15 0.5 ohm.

The oxygen concentration detector was heated by applying an alternating current to the first electric conductor 2 through the third electric conductors 3 connected thereto from an AC power source 20 producing
20 a 1 kHz output voltage of 2 V with a sinusoidal waveform. The temperature of the second electric conductor 6 reached 400°C in one minute after starting the application of the alternating current.

The output from the AC power source 20 was
25 rectified by a diode 28 connected to a resistor 29, and the thus rectified DC voltage was applied across the anode 24 and the first electric conductor 2, so as to prevent the oxidation of the first electric conductor 2

and to stabilize the potential thereof as a reference electrode potential.

The performance of the oxygen concentration detector was tested by placing it in an exhaust gas of 200°C from an automobile engine. The concentration of oxygen in the exhaust gas, or the concentration of that component of a fluid being measured which causes an electrode reaction, was determined by measuring the electromotive force across the second electric conductor 6 and the first electric conductor 2 by a potentiometer 21. The result showed that the electromotive force was 70 mV in an exhaust gas with an air-fuel ratio λ of 0.95, and 820 mV in an exhaust gas with an air-fuel ratio λ of 1.05. No deterioration was noticed at all after continuously using the oxygen concentration detector in the automobile exhaust gas for 500 hours.

Example 2

A 1 mm thick planar zirconia green body was prepared by using a mixture consisting of 100 parts by weight of powder material containing 92 mole % of zirconia (ZrO_2) and 8 mole % of ytterbium oxide (Yb_2O_3), 1 part by weight of clay as a sintering aid, and 18 parts by weight of binder including 12 parts by weight of polyvinyl butyral and 6 parts by weight of dioctyl phthalate.

Referring to Fig. 10, a first electric conductor 2 and third electric conductors 3 were formed on one side surface of the thus prepared planar green

body by the screen printing method while using a paste containing 95% of alloy powder and 5% of zirconia powder, which alloy powder included 80% of platinum and 20% of rhodium. A first 0.3 mm thick planar zirconia green body layer with the same chemical composition as that of the above-mentioned 1 mm thick planar green body was overlaid on said one side surface of the planar green body, while forming hollow spaces 5 so as to expose a part of the first electric conductor 2 to the hollow spaces 5. Separately, a second 0.3 mm thick planar zirconia green body layer with the same chemical composition as that of the above-mentioned 1 mm thick planar green body was prepared, and second electric conductors 6 were formed thereon by printing a paste containing 95% of platinum powder and 5% of zirconia powder. The second 0.3 mm thick green body layer with the second electric conductors 6 was overlaid on the first 0.3 mm thick green body layer. To form a gastight layer 25, a third 0.3 mm thick zirconia green body layer with the same chemical composition as that of the above-mentioned 1 mm thick planar green body and having a cavity 38 was overlaid on the second 0.3 mm thick green body layer. A fourth 0.3 mm thick zirconia green body layer 36 with the same chemical composition as that of the above-mentioned 1 mm thick planar green body and having a gas diffusing hole 37 of 0.15 mm diameter was overlaid on the third green body layer for the gastight layer 25. The thus assembled green bodies

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were sintered at 1,450°C in air, so as to produce an oxygen concentration detector of the invention.

The thus produced oxygen concentration detector was heated by applying an alternating current to the first electric conductor 2 through the third conductors 3 connected thereto, capacitors 27, and AC ammeter 31, and an inductor 30 from an AC power source 20 producing a 40 kHz output voltage of 6 V with a rectangular waveform. The temperature of the second electric conductor 6 reached 730°C in 20 seconds after starting the application of the alternating current. The magnitude of the alternating current during the heating was 0.5 A, and this magnitude of the current proved to respond very quickly to changes in the outdoor temperature with a very high sensitivity.

The performance of the oxygen concentration detector was tested by placing it in a gas consisting of 95% of nitrogen (N_2) and 5% of oxygen (O_2) at 50°C. The oxygen concentration was determined by applying a direct current across the first electric conductor 2 and the second electric conductor 6 facing the gas diffusing hole 37 from a DC power source 34 through a resistor 29 and a DC ammeter 31D, until almost all oxygen in the cavity 38 was transferred to the hollow spaces 5 so as to cause the oxygen concentration in the cavity 38 to vanish to substantially zero, and measuring the magnitude of the direct current when the potential difference between the two second electric conductors 6

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and the first electric conductor 2 varied suddenly in response to the vanishing-to-zero of the oxygen concentration in the cavity 38. The result showed that the direct current at the vanishing-to-zero of the oxygen concentration in the cavity 38 was 10 mA. Thus, the oxygen concentration detector of this example proved to be practicable as a detector including an oxygen pump.

Example 3

A tubular solid electrolyte 1 with an outside diameter of 8 mm and an inside diameter of 6 mm as shown in Fig. 9 was prepared by using a proton-conductive electrolyte having a chemical composition of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$. A first electric conductor 2 and third electric conductors 3 both made of nickel were deposited on the outer surface of the tubular solid electrolyte 1 by the high-frequency sputtering method. The resistance across opposite ends of the first electric conductor 2 was 1 ohm, while the resistance of the third electric conductors 3 was 0.2 ohm. A second electric conductor 6 was formed by applying a film of nickel paste on the inside surface of the tubular solid electrolyte 1 by brushing and firing the thus applied nickel paste film at 1,000°C in a nitrogen atmosphere.

The first electric conductor 2 was heated by applying an alternating current thereto through the third electric conductors 3 from an AC power source 20 producing a 100 kHz output voltage of 10 V with a rectangular waveform. Consequently, the temperature of the solid

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electrolyte 1 reached 620°C in three minutes after starting the application of the alternating current. On the other hand, a direct current of 10 mA was applied across the first electric conductor 2 and the second
05 electric conductor 6 from a DC power source 34 through a resistor 29, while passing dry oxygen through the inside space of the tubular solid electrolyte 1 at a rate of 10 ml/minute and exposing the outside of the solid electrolyte 1 to the open air. As a result, 0.7%
10 of water was produced in the oxygen gas downstream of the inside space of the tubular solid electrolyte 1, which proved that the amount of proton which corresponded to the electric charge transmitted by the direct current moved from the first electric conductor 2 to the second
15 electric conductor 6 through the solid electrolyte 1 so as to produce water by reacting with the oxygen flowing through the inside of the solid electrolyte 1. Thus, it was confirmed by tests that the device of this example can be used for controlling the moisture in the
20 gas flowing through the inside of the tubular solid electrolyte 1.

As described in detail in the foregoing, the electrochemical device and cell and the method of operating the cell according to the present invention
25 are simple in construction yet highly effective in facilitating very quick heating of a solid electrolyte from a low temperature by using a low AC power source voltage, so as to provide excellent low-temperature

performance of the electrochemical device and cell.
Besides, the device and the cell of the invention are highly durable, because the solid electrolyte thereof is free from deterioration even after repeated heating.

05 The electrochemical device and the cell can be used for detecting and controlling that component of a fluid which causes an electrode reaction in the cell. Examples of such component to be detected or controlled are oxygen, nitrogen, carbon dioxide gas, hydrogen, and

10 sodium, but the invention is not restricted to such examples. Especially, the electrochemical device can be advantageously used as an oxygen concentration detector for exhaust gas from internal combustion engines, because the device can accurately determine

15 the oxygen concentration of the exhaust gas at low temperature immediately after starting the engine or during low-speed running thereof. Accordingly, the present invention is very useful for detection and control of concentration of certain substances in

20 various industries, especially in preventing air pollution caused by engine exhaust gas.

Although the invention has been described with a certain degree of particularity, it is understood that the present disclosure has been made only by way

25 of example and that numerous changes in details of construction and the combination and arrangement of parts may be resorted to without departing from the scope of the invention as hereinafter claimed.

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CLAIMS

1. An electrochemical cell having a solid electrolyte (1) and first and second electric conductors (2,6), characterised in that the first electric conductor (2) is in direct contact with the solid electrolyte (1),
5 the second electric conductor (6), which is to be exposed to a fluid including a component to be detected or controlled, is in direct contact with the solid electrolyte (1) at a spacing from the first electric conductor (2), and in that means (3) are provided to connect an AC power
10 source across at least one of said first and second electric conductors, whereby said electrochemical cell can be heated, in use, and when heated be used to detect and/or control the concentration of the component of the fluid in contact therewith with component causes an
15 electrode reaction at the electrochemical cell.

2. An electrochemical cell according to claim 1, characterised in that the first electric conductor (2) is embedded in or secured to the surface of said solid electrolyte (1).

20 3. An electrochemical cell according to claim 1 or 2, characterised in that at least one of said first and second electric conductors (2,6) forms at least one electrode of the electrochemical cell.

25 4. An electrochemical cell according to claim 1, 2 or 3, characterised by third electric conductors (3) in direct contact with the solid electrolyte (1) and

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connected to opposite ends of at least one of said first and second electric conductors (2,6), said third electric conductors (3) being adapted to be connected to said AC power source and having an electric resistance which is smaller than that of said first and/or second electric conductor to which they are connected.

5 5. An electrochemical cell including an electrolytic cell and a concentration cell, characterised in that the electrolytic cell consists of a pair of electrodes secured to respective surfaces of a solid electrolyte and the concentration cell consists of a pair of electrodes secured to respective surfaces of the solid electrolyte or another solid electrolyte electrically conductively connected thereto; in that a heater made of a conductor is secured to the or one of the solid electrolytes or to a further solid electrolyte electrically conductively connected thereto; and in that a cavity or porous layer is adjacent a surface of the or each solid electrolyte with electrodes thereon, and allows access to such surface(s) with a given diffusion resistance of a fluid to be detected, one electrode of each of the electrolytic and concentration cells being provided so as to face the cavity or porous layer.

25 6. An electrochemical cell according to claim 5, characterised in that the maximum value of DC resistance between the separated electrodes positioning on the common side of the solid electrolyte is larger than DC resistance between the electrodes of the

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electrolytic cell.

7. An electrochemical cell according to claim 5 or 6, characterised in that the solid electrolytes are laminated and in that, when there are two, they are electrically conductively connected.

8. An electrochemical cell according to claim 5, 6 or 7, wherein there are two solid electrolytes with electrodes thereon, characterised in that the cavity or porous layer is provided between the first solid electrolyte and the second solid electrolyte.

9. An electrochemical cell according to any one of claims 5 to 8, characterised in that the electrodes of the electrolytic cell and the concentration cell positioning on one side of the solid electrolyte and/or facing the cavity or porous layer are common.

10. An electrochemical cell according to any one of claims 5 to 9, characterised in that said heater is one of the electrodes of one of the cells.

11. An electrochemical cell according to any preceding claim, characterised in that the or each solid electrolyte is oxygen-ion-conductive so that the electrochemical cell in use detects the oxygen concentration in a gas in contact therewith.

12. A method of operating an electrochemical cell having first and second spaced electric conductors tightly secured to a solid electrolyte with one conductor being exposed to a fluid including a component to be detected or controlled, characterised by the step of

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passing an alternating current through at least one of
said electric conductors so as to heat the electrochemical
cell, and detecting or controlling the concentration of
that component, which component causes an electrode
5 reaction at said electrochemical cell.

13. A method according to claim 12,
characterised in that said alternating current has a
frequency sufficiently high that the interface impedance
between said solid electrolyte and the electric conductor
to which alternative current is passed is largely
10 independent of the interface capacitance therebetween.

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FIG. 3

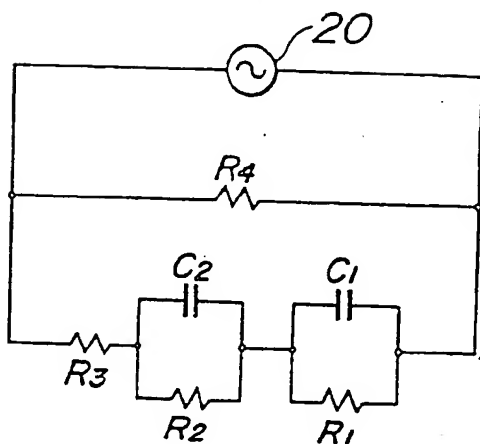


FIG. 4

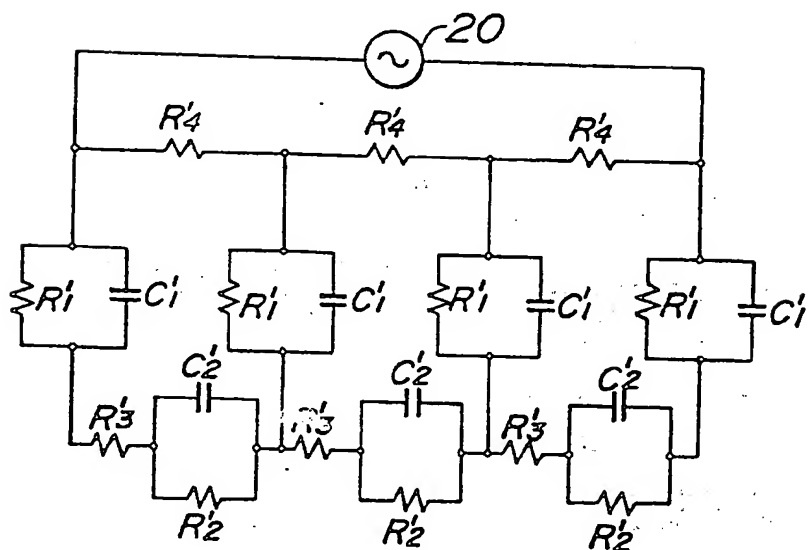
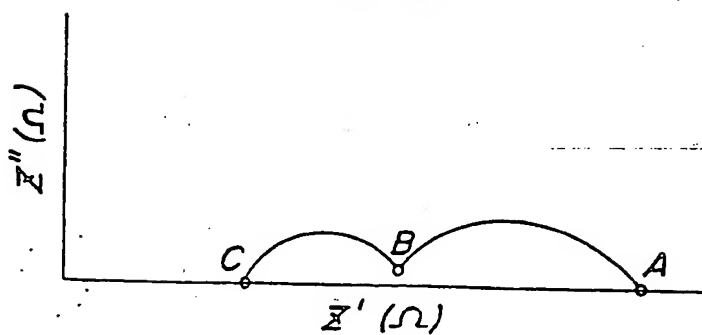


FIG. 5



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FIG. 6

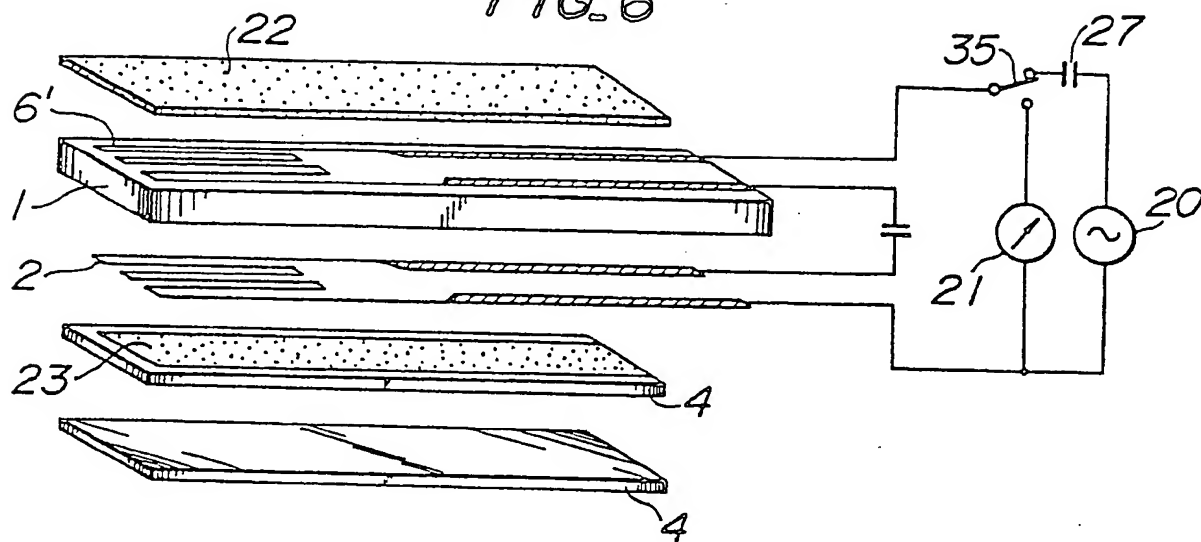


FIG. 7

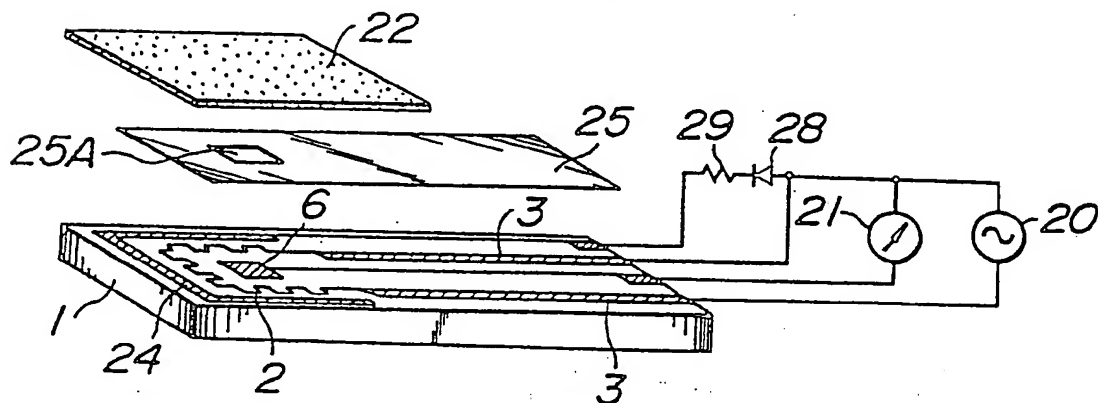
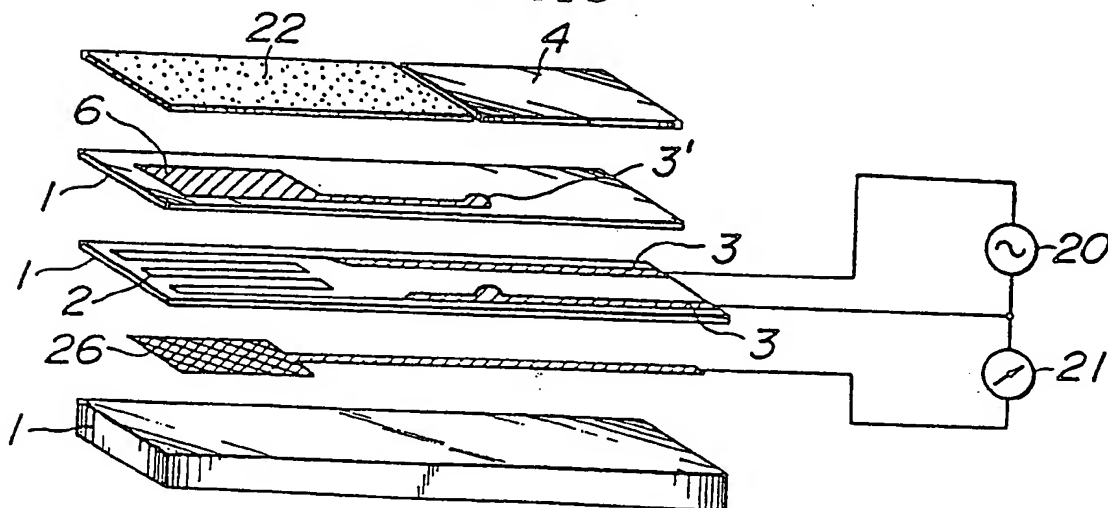


FIG. 8



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FIG. 9

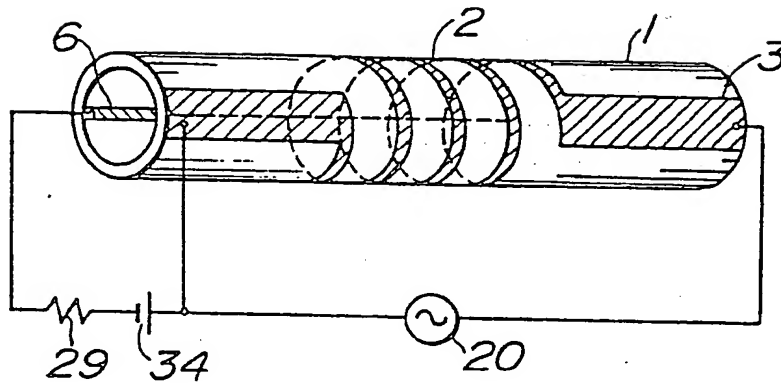
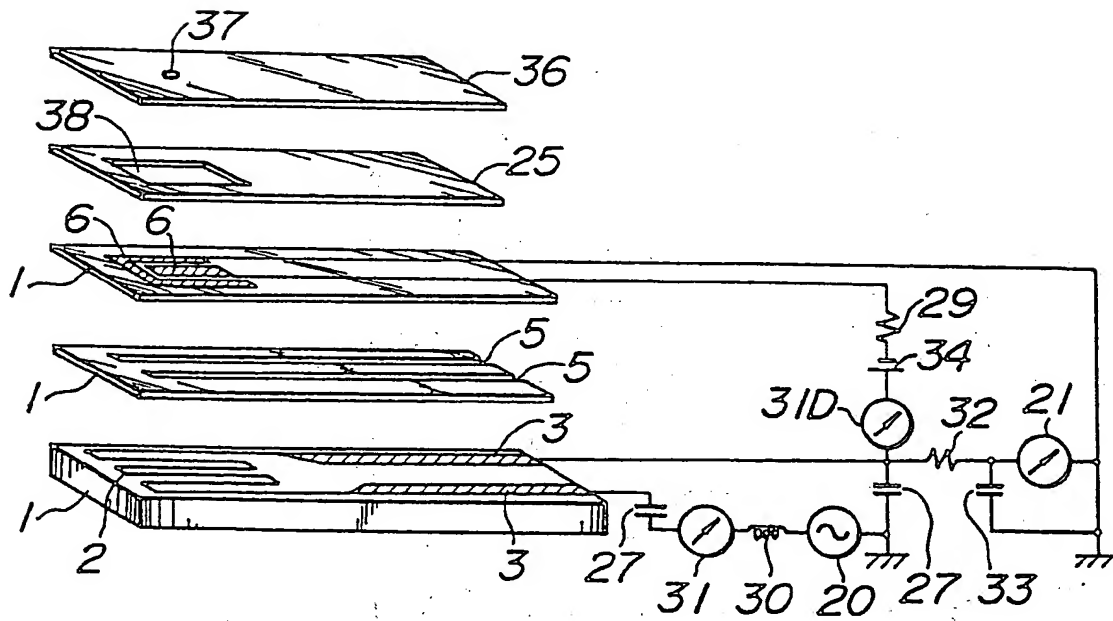


FIG. 10



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FIG. 13

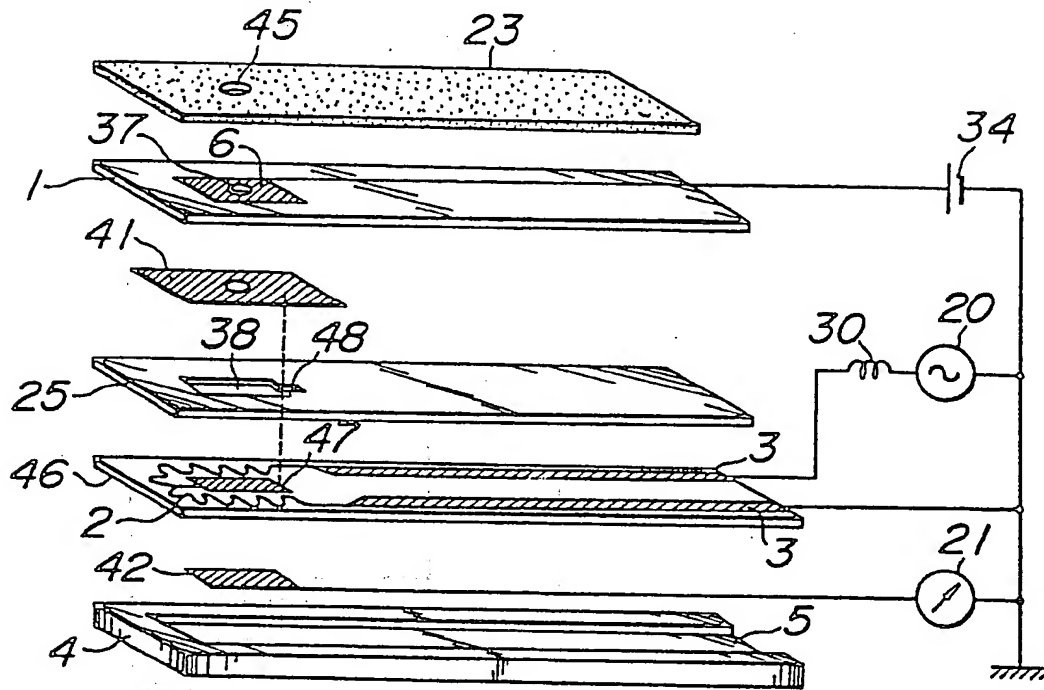
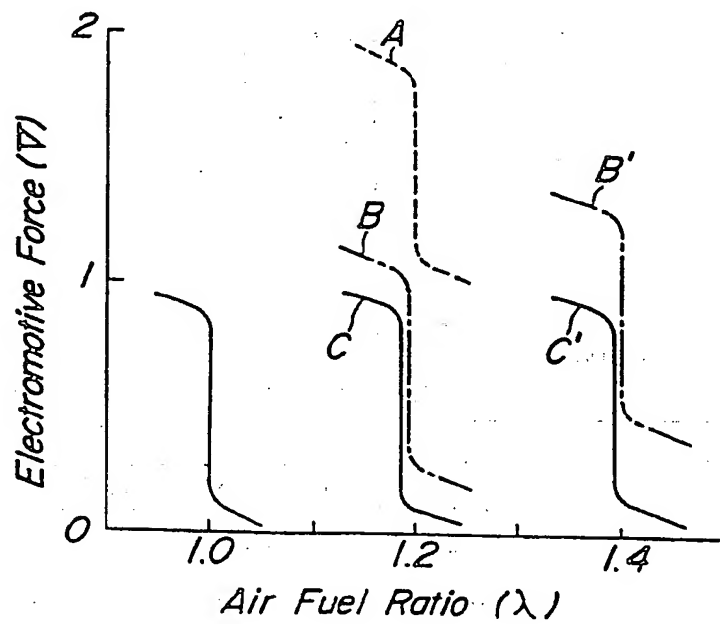


FIG. 14





European Patent
Office

EUROPEAN SEARCH REPORT

0108179

Application number

EP 82 30 6646

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. *) |
| X | EP-A-0 030 164 (NGK INSULATORS) * Figures 1, 5; page 5, line 25 - page 6, line 23; page 7, lines 17-23 * | 1-3, 12 | G 01 N 27/56 |
| Y | EP-A-0 035 400 (FORD MOTOR) * Figure 5A; page 8, line 15 - page 9, line 6; page 12, lines 6-34 * | 5 | |
| A | * Figure 5A; claim 3 * | 7, 8, 11 | |
| Y | GB-A-2 054 868 (R. BOSCH) * Figure 4; page 4, lines 32-83 * | 5 | |
| A | EP-A-0 057 899 (HITACHI) * Abstract * | 5 | TECHNICAL FIELDS SEARCHED (Int. Cl. *) |
| A | GB-A-2 057 140 (NISSAN MOTOR) * Abstract * | 5 | G 01 N 27/56 G 01 N 27/58 |
| The present search report has been drawn up for all claims | | | |
| Place of search BERLIN | | Date of completion of the search 05-01-1984 | Examiner DEVEZA R.R. |
| CATEGORY OF CITED DOCUMENTS | | | |
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